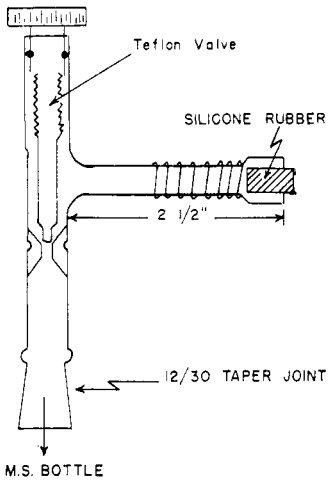

Figure 2. Improved inlet valve

carbon absorption on the valve itself must be negligible.

The arithmetic procedures for correcting the mass spectrum of total naphtha for the contributions of the C_5 and lighter components obtained by gas chromatography, are shown below. After correction for light ends, the hydrocarbon-type analysis is computed in the usual manner (*1*).

The mass spectrum of the total naphtha is obtained, and the pressure is recorded. The pressure is corrected for any air that may be present. An approximate hydrocarbon-type analysis is then calculated (*1*). Using the average carbon numbers of the paraffins and the alkylbenzenes, the approximate density of the C_{6+} portion of the sample can be calculated.

$$\text{Density}_p = 0.66 + 0.02\ (\text{carbon number}_p - 6)$$
$$\text{Density}_{cyp} = 0.75 + 0.01\ (\text{carbon number}_p - 6)$$
$$\text{Density}_{ab} = 0.876$$

where p indicates paraffins, cyp indicates cycloparaffins, and ab indicates alkylbenzenes.

First approximate density of C_{6+} =

$$\frac{\%\ p \times \text{density}_p + \%\ cyp \times \text{density}_{cyp} + \%\ ab \times \text{density}_{ab}}{\Sigma\%\ p,\ cyp,\ ab}$$

From the carbon numbers of the paraffins and alkylbenzenes and the approximate type analysis, the molecular weight of the C_{6+} can be computed.

Approximate MW of C_{6+} =

$$\frac{\%\ p\ [86 + 14\ (\text{carbon number}_p - 6)] + \%\ cyp\ [84 + 14\ (\text{carbon number}_p - 6)] + \%\ ab\ [78 + 14\ (\text{carbon number}_{ab} - 6)]}{\Sigma\ \%\ p,\ cyp,\ ab}$$

The volume percentages of light components determined by gas chromatography are multiplied by appropriate volume-mole factors and normalized to the total microns of air-free sample. The molar contribution of each light component is calculated at masses 41, 43, 55, 57, 67, 69, and 71. The hydrocarbon-type analysis is then recalculated, using Σ values corrected for the light components.

To demonstrate the validity of the method, samples were analyzed by low temperature fractional distillation and mass spectrometry (Table I). The C_{6+} portions were introduced into the mass spectrometer through a heated indium-covered sintered disk and the results were compared with those obtained using the gas chromatograph–mass spectrometer method.

With the present method, no loss in accuracy or reproducibility was experienced, and a considerable amount of costly distillation time was eliminated.

ACKNOWLEDGMENT

The authors express appreciation to J. Colucci for assistance in obtaining the mass spectra.

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Gas Chromatography of Food Volatiles—An Improved Collection System

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GAS CHROMATOGRAPHIC ANALYSIS of trace volatiles that contribute flavor to foods requires preliminary concentration. Collection and concentration are effected by passing a stream of air or nitrogen over the samples and condensing the volatile compounds in a packed or unpacked refrigerated trap (*2*, *5*, *6*). Nawar and Fagerson (*4*) in an effort to improve the efficiency of the freeze-out process have recycled air or nitrogen in a closed system that incorporates a refrigerated trap. The collected volatiles are then heated to facilitate transfer and introduced onto the column through a series of valves or stopcocks. These techniques are cumbersome and during transfer material may be lost by condensation and adsorption on connecting surfaces; in addition, the subsequent decontamination of traps and valves represents a formidable problem.

It has also been suggested that, for quality control purposes, vapors above heated vegetables and food products can be sampled with a syringe and injected directly into the gas liquid chromatography (GLC) unit (*1*, *3*). Here, too, particularly at the high sensitivities required, contamination from the syringe and the septum in the heated injection port can lead to extraneous peaks in subsequent analyses unless additional bake-out or clean-up procedures are used.

The technique described here utilizes a refrigerated, stainless steel or copper coil filled with column material for the collection trap. Swagelok fittings are used to make this coil an integral part of the column. The chromatogram is obtained without any gas transfer systems and without the use of heated injection ports, and the collection coil itself can be used repeatedly without further cleanup.

EXPERIMENTAL

Apparatus. The gas chromatograph is an F&M Model 609 equipped with a flame ionization detector and incorporating linear temperature programming. The insulated column heating chamber is cylindrical, 7 inches i.d., and 7 inches in height. The columns described are fitted to these dimensions.

Columns are 7.5 feet long, packed with

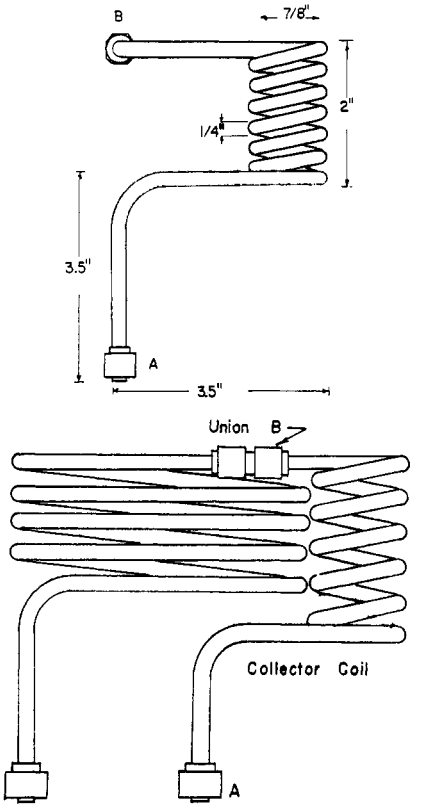

Figure 1. Collector coil and assembled GLC column

Top. Collector coil. A and B are Swagelok fittings. Coil may also be made of 0.125 inch o.d. tubing
Bottom. Assembled column. Note position of fittings A and B. A is at the end where sample was trapped

25% Castorwax on 30- to 60-mesh acid-washed Chromosorb W. Each column consists of two sections (Figure 1) joined by a Swagelok union (appropriate Swagelok fittings were used for all connections), a 5.5-foot section coiled into a helix, 5 inches i.d., and a 2-foot section coiled into a helix $^7/_8$ inch i.d. The ends of this small coil are so arranged that the coil can be conveniently suspended in a small Dewar flask (Figure 1).

Two columns were evaluated, one of stainless steel, 0.125 inch o.d., 0.075 inch i.d., and the other of copper 0.25 inch o.d., 0.19 inch i.d. Programming was at 4.6° per minute from 40° to 125° C., and heating was continued isothermally at 125° C. The nitrogen flow rate was 12 ml. per minute for the 0.125-inch o.d. column and 50 ml. per minute for the 0.25-inch o.d. column, hydrogen flow rate was 40 ml. per minute, and the air flow rate was 450 ml. per minute.

A good base line with these operating parameters could be obtained at a sensitivity setting equivalent to full scale pen deflection, on the 1-mv. Brown recorder, for approximately 1×10^{-11} ampere. In preparing columns the entire 7.5-foot length was packed, aged until satisfactory, and then a 2-foot length cut off and made into the collection coil.

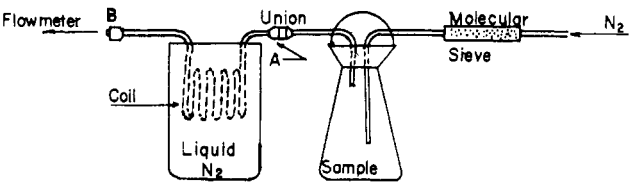

Figure 2. Assembly for collection of volatiles. Note position of fittings A and B. A becomes the start of the assembled column

METHOD

A weighed amount of sample was placed in a 250-ml. Erlenmeyer flask. The assembly for collecting volatiles is shown in Figure 2. The sweep gas, usually water-pumped nitrogen, was purified by passage through a Linde molecular sieve (5 A.) column. With wet samples—e.g., ground meat—a drying tube containing anhydrous sodium sulfate, to remove the bulk of the water in the gas stream, backed by $CaSO_4$, to complete the drying, was placed between the sample and the collection coil. With fatty materials this precaution was omitted. In either case the exit tube leading to the collection coil was thick-walled glass tubing 0.25 inch o.d. ending in a 0.25-inch fitting. The back ferrule of this fitting was a silicone rubber gasket (made from a septum used for the injection port of the gas chromatograph). A 0.25-inch union was used to connect to the 0.25-inch o.d. collection coil, and a 0.25-inch to 0.125-inch reducer was used to connect to the 0.125-inch o.d. collection coil. This coil was immersed in a Dewar flask containing liquid nitrogen. The exit of the coil was attached to a drying tube, and this, in turn, to a soap bubble flow meter. Flow rates were between 30 to 60 ml. per minute, and sampling times between 15 and 60 minutes. At the completion of a run, the nitrogen flow was stopped. The exit end of the collection coil was immediately coupled to the main section of the column. The connection to the sample flask was detached and this end of the coil sealed with a Swagelok plug. The coil was removed from the liquid nitrogen, the plug serving to keep the expanding gas from mechanically carrying any of the trapped volatiles out of the column. The plug was then removed and the composite column attached to the ports in the heating area. A slight positive nitrogen pressure was applied and the flame ignited. After 5 minutes the nitrogen flow was adjusted to the desired rate and the temperature programming started.

RESULTS AND DISCUSSION

Preliminary trials showed that a packed coil was more efficient than a packed U-tube in trapping volatiles, even at liquid nitrogen temperatures. The possibility remained, however, that resolution might be impaired either by the tightly wound helix of the collection coil or by the approximately 1.5-inch break in the column packing at the junction of the two coils. A mixture of acetone (b.p. 56.5° C.) isopropanol (b.p. 82.5° C.), propanol (b.p. 97–8° C.), isobutanol (b.p. 108° C.), and *n*-butanol (b.p. 117–18° C.) was prepared. To minimize errors in reproducing the sample size, a relatively large sample, 1 μl., was injected in the conventional manner and chromatographed with programming at an appropriate sensitivity. A similar sample was carried through the trapping procedure and the collection coil was joined to the main portion of the column and chromatographed in identical fashion. The two curves are shown in Figure 3. Peak heights and peak areas are almost identical, and peak widths for the sample trapped in the coil are perhaps 5% wider at the acetone peak and almost 10% narrower by the time the *n*-butanol peak is reached. Presumably the lowest boiling component was trapped out in a slightly larger volume than the highest boiling component. In Figure 4, chromatograms are shown for the volatiles trapped at liquid nitrogen temperature from lamb fat heated to 100° C. for 30 minutes. The chromatogram obtained from the volatiles trapped in a 0.125-inch stainless steel collection coil and then incorporated as an integral part of the column is far more detailed than the chromatogram obtained by trapping the volatiles in a

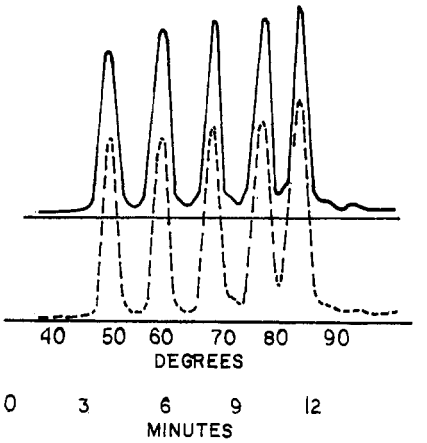

Figure 3. Separation of mixture boiling range 56.5–118° C.

——— Collector coil
– – – – Sample injection

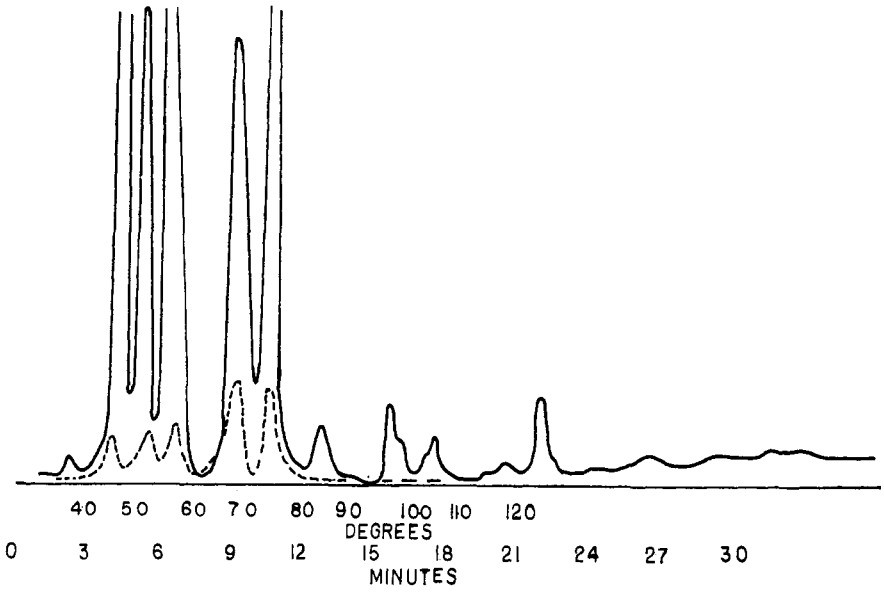

Figure 4. Volatiles trapped from heated lamb fat

———Collector coil
.....Conventional freeze-out procedure and transfer

U-tube and transferring in a conventional manner. Comparative runs with other meat products gave similar results.

The use of the trapping coil as an integral part of the column lends itself readily to temperature programming, which is preferable to use in flavor studies because the boiling range of the volatiles is so great that isothermal analyses lead to peak crowding at the start of the analyses and to excessive peak broadening at the end of the run. The collection coil need not contain the same column packing as the body of the column; it may in some instances be advantageous to have a preliminary separation on the collection coil and a follow-up separation on the main coil. Although we have used both 0.25- and 0.125- o.d. columns, we prefer the narrower columns. Separations are perhaps more efficient, trapping coils are compact, higher programming temperatures can be used, and there is a saving in carrier gas and column packing.

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Detachable Auxiliary Sheets for Easy Detection of Bands on an Electrophoresis Curtain

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IN THE CONTINUOUS-FLOW electrophoresis apparatus, the paper curtain is fastened to the electrode wigs so that it can not be removed readily for detection of the bands. As a result, the bands on the curtain can be detected only either by rendering the sample visible in daylight or ultraviolet light before electrophoresis or by spraying the curtain with coloring reagents after electrophoresis. The former method may make difficult further chemical analyses of the separated compound for its identification, while the latter is time-consuming, discontinuous, and uneconomical.

The present technique employs auxiliary sheets prepared from rectangular pieces of filter paper of about 4 × 5 inches or larger which are cut from a large sheet with a spatula or the blunt edge of a knife. After being wetted with the electrolyte solution in use, an auxiliary sheet is applied, lower edge first, on any desirable location on the wet curtain as shown in Figure 1. The application can be carried out before or during electrophoresis after electric current is disconnected and level of electrolyte in the reservoir temporarily lowered. It is important that operation in removing and replacing the front cover plate of the apparatus and reconnection of electric current be done rapidly to avoid damages to the band pattern. The auxiliary sheet absorbs the bands without altering their pattern on the curtain.

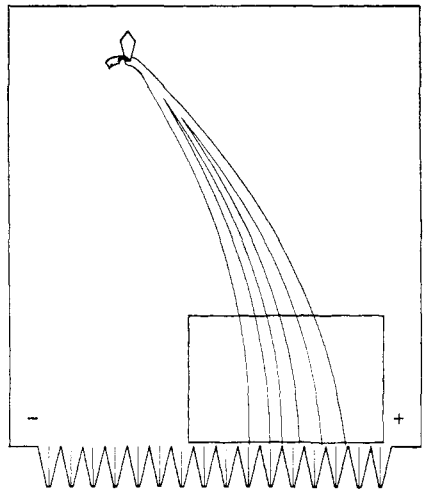

Figure 1. An auxiliary sheet as adhered on the curtain of Spinco Model CP continuous-flow paper electrophoresis apparatus

After absorption and disconnection of electric current, the auxiliary sheet is detached from detection of bands by lifting one corner of it either with a spatula or by applying gentle suction.

The advantages in using these auxiliary sheets are numerous. Preliminary study of fractionation of the sample can be conducted directly in the apparatus under operational conditions by spotting the sample on the auxiliary sheet. The exact location of invisible bands can be determined by spraying the auxiliary sheets containing absorbed bands with specific reagents, while the electrophoresis process is virtually uninterrupted. Thus, proteins can possibly be fractionated without staining. Conditions for adjustment of the apparatus for best electrophoresis pattern of invisible compounds can be determined by studying auxiliary sheets applied directly under the sample application tab on the curtain. For the determination of an unknown compound, a large number of absorbed auxiliary sheets can readily be prepared for various chemical treatment. It makes possible the detection of bands with corrosive reagents—e.g., concentrated sulfuric acid—by using glass fiber paper as auxiliary sheets.

[1] Florida Agricultural Experiment Station Journal Series, No. 1353.